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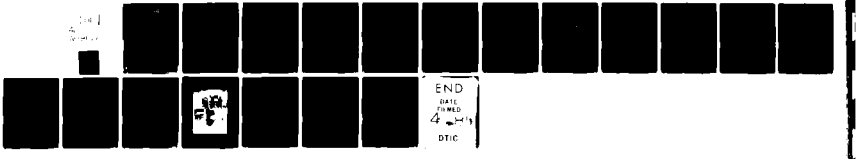

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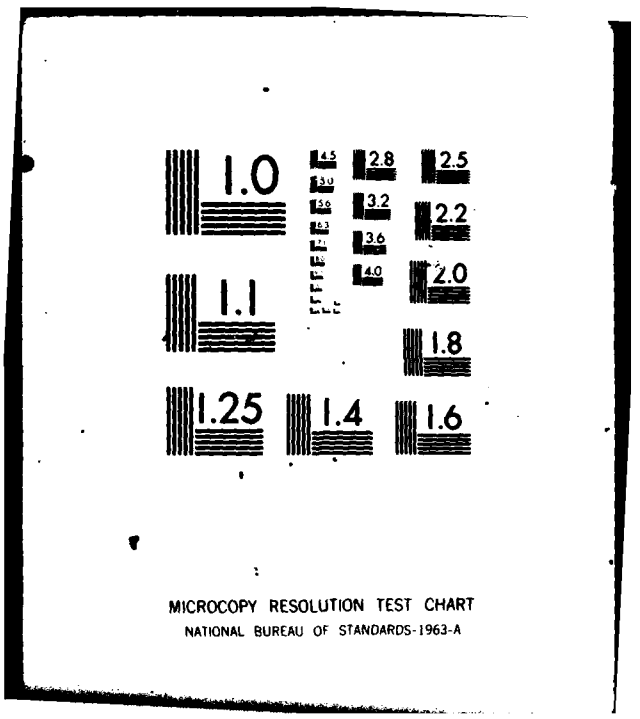
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EXOTHERMIC IR SOURCE MATERIALS
LITHIUM - BORON ALLOY MATERIALS

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30 September 1980

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The preparation of a lithium-boron compound alloy is discussed. Its reactivity with an ambient atmosphere, and with dry and humid atmospheres of air, oxygen, and nitrogen is presented and compared to the reactivity of lithium metal under similar conditions.

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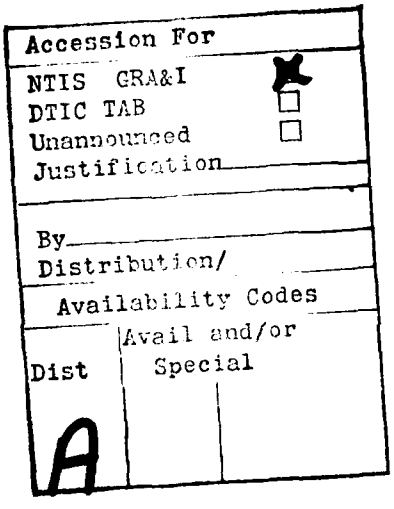
PREFACE†

This report of NAVAIR sponsored research includes work done at both Naval Surface Weapons Center (NAVSWC), White Oak, and Naval Weapons Support Center (NAVWPNSUPPCEN), Crane. The NAVSWC personnel were Dr. F. Wang and Dr. R. Sutula; those at NAVWPNSUPPCEN Crane were Dr. H. Lewis and Dr. H. Webster.



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†In order to specify procedures adequately, it has been necessary to identify commercial materials and equipment in this report. In no case does such identification imply recommendation or endorsement by the Navy, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

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1. INTRODUCTION

Recently, during investigation into the formation of alloys of lithiumfor potential use as battery electrodes, Wang et. al.[1,2,3] reported the formation of an unusual compound-alloy between lithium and boron. The compound reported has the formula Li_5B_4, is totally metallic in properties, and is chemically reactive in air. This last property made the alloy useless for a battery electrode. In conjunction with Dr. Wang, research personnel at Crane have pursued investigations into the formation and reactivity of lithium-boron compound alloys.

2. RESEARCH OBJECTIVES

The objectives of this research have been and continue to be the investigation of the reaction processes which lead to the formation of lithium-boron, alloys to characterize the composition of the alloy materials to determine the phase equilibria and plot the phase diagrams, and to ascertain the reactivity of the alloys with the ambient environment.

3. DISCOVERY OF ALLOY MATERIALS

The solubility of boron in lithium had been reported as rather small*, but Wang[3] observed that above 300°C crystalline boron readily dissolves in molten lithium (Figure 1).†

---

1. F. E. Wang, M. A. Mitchell, R. A. Sutula, J. R. Holden, and L. H. Bennett, J. Less-Common Metals, 1978, 61, 237.

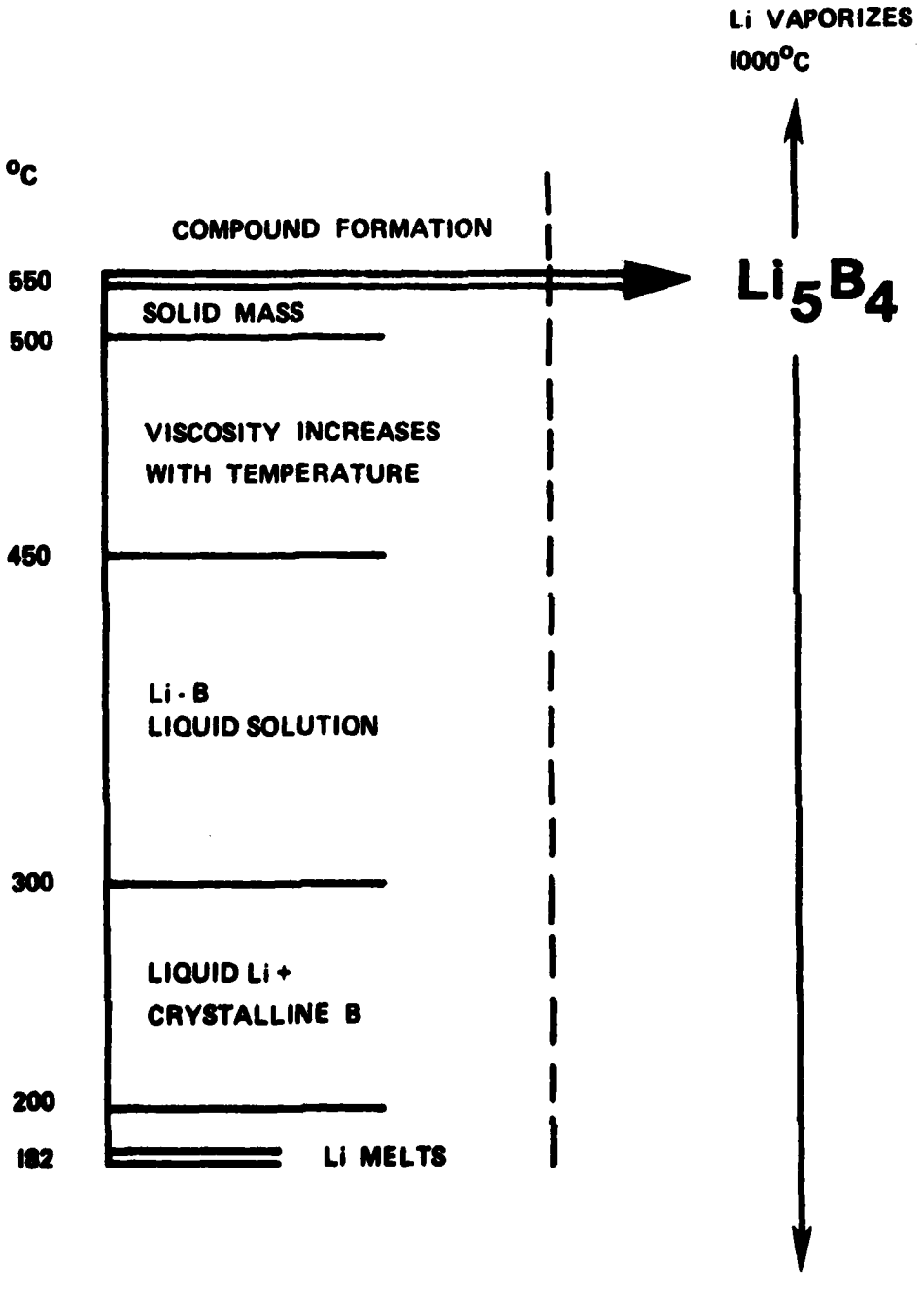
2. J. R. Letelier, Y. N. Chiu, and F. E. Wang, ibid., 1979, 67, 179.

3. F. E. Wang, Metal. Soc. AIME J., Metal. Trans. A, 1979, 10A, 343.

*cf. Reference 3, and references contained therein.

†Courtesy Dr. F. E. Wang (cf. Reference 3).

FIGURE 1. Thermal History of Li-B Compositions



In fact, up to 40 at. pct. solution of boron in lithium was easily attained. When such solutions were cooled to ambient temperatures however, the latent heat of freezing lithium was evolved.

When a solution containing between 10 and 40 at. pct. boron was heated above 400°C, the viscosity of the solution gradually increased until, at about 500°C, the solution solidified. If such a system was then cooled to ambient temperature, it became liquid again and then evolved the heat of fusion of lithium as before. However, when an attempt was made to melt the solid phase formed at 500°C by further heating, a vigorous exotherm occurred at about 550°C in the solid phase. Subsequent heating to about 1000°C did not yield a melt, but only vaporization of lithium from the solid phase. Upon cooling a solid composition which had gone through the exothermic process, a much reduced heat of fusion of lithium was observed, and at a composition corresponding to Li_5B_4, cooling to ambient temperature yielded no heat of fusion, indicating that a new compound existed at that composition. Subsequent studies verified this speculation.[1,2]

4. AIR REACTIVITY OF COMPOUND-ALLOY

As mentioned previously, the compound-alloy is chemically reactive with ambient environments, becoming quite warm to the touch. The various compositions produced thus far have all been metallic solids much like lithium itself; consequently, they must be machined to produce small pieces. Therefore, from four different compositions, disks 3.5cm dia. x 2.5cm were cut and their reaction with ambient environment was monitored as temperature change with time. The thermal histories obtained are shown in Figure 2.† Sample temperatures were recorded at one-half minute intervals during the first fifteen minutes of reaction time, and every minute thereafter.

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†From data supplied by Dr. F. E. Wang

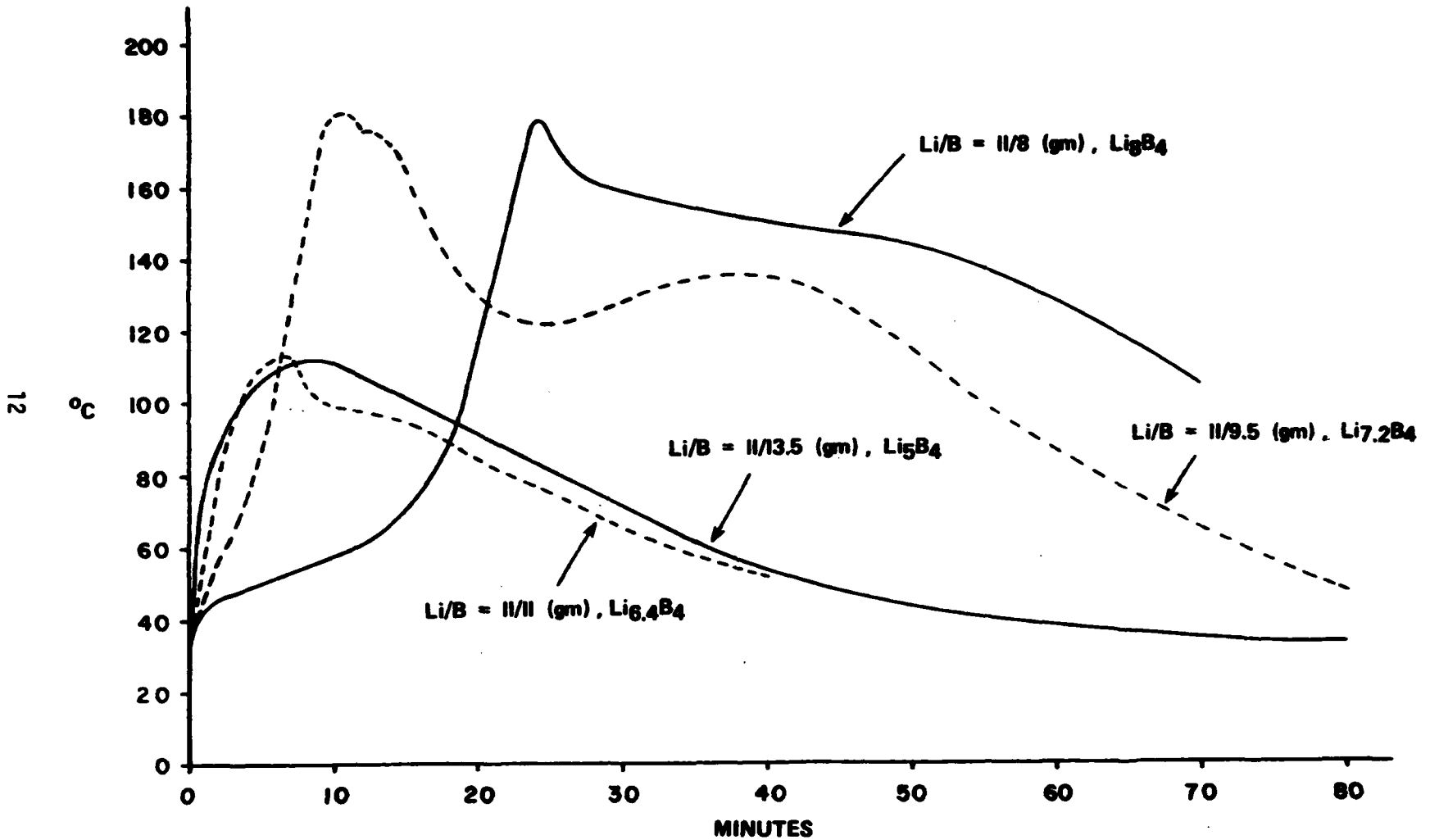

FIGURE 2. Temperature vs. Time Plots for Li-B Alloy Reactivity With Ambient Air

The most lithium rich samples, corresponding to Li_8B_4 and $Li_{7.2}B_4$, exhibited temperature maxima of 180°C, although Li_8B_4 showed an induction period, and $Li_{7.2}B_4$ went through two temperature maxima but did not show an induction period. The other two samples, with compositions $Li_{6.4}B_4$ and Li_5B_4, appeared to be less reactive, reaching lower temperature maxima of about 110°C.

Although a seemingly sharp difference in thermal behavior for the samples occurred, the reasons for such a difference are not obvious. Also, the temperature maximum of 180°C, although corresponding to the fusion temperature for lithium metal, would seem to be an artificial barrier, for if lithium is melting within the solid phase its air reactivity should be enhanced. Thus these data must be regarded as very qualitative in nature.

In order to obtain more information on the alloy reactivity with ambient environments, a more controlled reactivity study was needed. Using milled shavings from a composition $Li_{8.8}B_4$ produced at NAVSWC White Oak, the reactivity of the sample with various flowing atmospheres was studied at NAVWPNSUPPCEN Crane. The shavings were loaded into a ceramic boat (usually 0.15-0.20gm) inside a glove box with an argon purge, and these were placed in a 25mm glass tube fitted with gas inlet and outlet tubes. Then, via connections to the external world, a desired atmosphere could be circulated over the sample without interfering with the glove box atmosphere. Temperature in the sample was monitored with a thermocouple buried in the alloy shavings.

When either dry air, dry nitrogen, or dry oxygen was the atmosphere circulating over the sample, no temperature change with time was observed over periods of up to four hours. However, when moist air prepared by passing dry air through a water column at ambient temperature was used, an immediate temperature change occurred in the sample as shown in Figure 3a, which is a typical result. When moist oxygen was used, results such as shown in Figure 3b were obtained, and if moist argon or moist nitrogen was used,

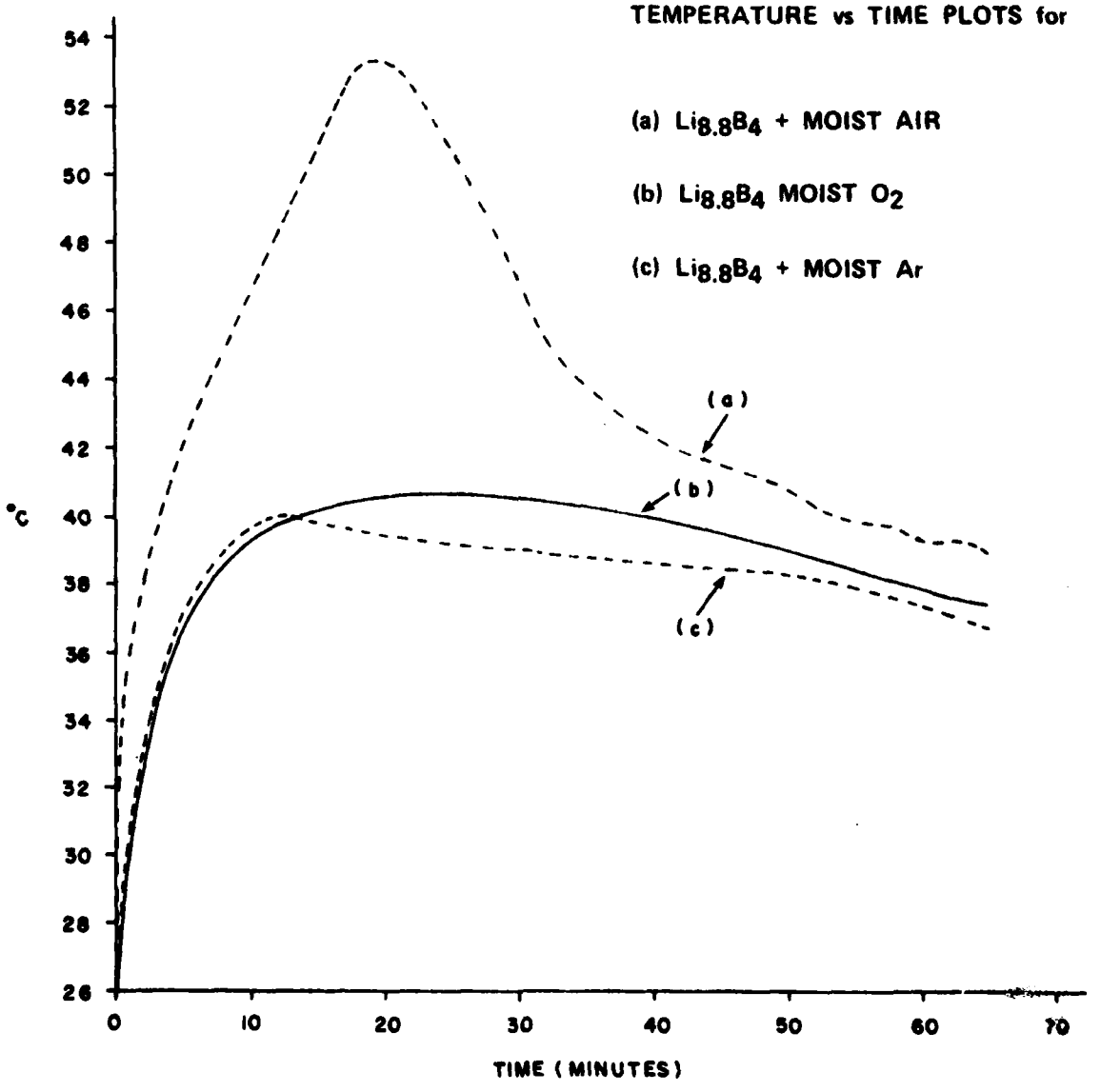

FIGURE 3. Temperature vs. Time Plots for Li-B Alloy Reactivity With Controlled Atmospheres

curves such as Figure 3c were obtained. The similarity between (b) and (c) is apparent. No explanations are as yet evident. The shavings typically changed from grey in color and flexible to black and brittle during exposure to moist environments. They eventually crumbled to a black powder. When partially reacted samples were added to water, some bubbling occurred, and eventually a black powder formed which gradually drifted to the bottom of the container.

5. AIR REACTIVITY OF LITHIUM METAL

The behavior of the alloy shaving samples discussed above was reminiscent of the reported air reactivity of lithium metal.[4,5] For comparison purposes, lithium ribbon samples of 0.15-0.20gm were subjected to studies as above. The lithium metal was purchased from Ventron Division of Thiokol Corp., Alfa Products, as 0.38mm thickness ribbon packed under argon, which was cut into small sections about 2mm x 2cm for these studies.

The lack of reactivity toward dry air, oxygen, and nitrogen was first confirmed. Then moist air was introduced as the circulating atmosphere, and the temperature versus time behavior plotted in Figure 4a was observed. The appearance of two exotherms with the second always larger than the first is particularly noted. The data presented are typical of these results and continued exposure to the circulating atmosphere produced no further temperature change, up to eight hours of time. When moist oxygen, nitrogen or argon was used as the atmosphere over the samples, Figure 4b was the typical result. Furthermore, introduction of moist nitrogen following the initial exotherm in a sample first subjected to moist oxygen, or vice-versa, did not cause a second exotherm.

---

4. J. C. Bailar, Jr., H. J. Emeleus, Sir R. Nyholm, and A. F. Trotman-Dickenson, Comprehensive Inorganic Chemistry, Volume 1, Pergamon Press, 1973, 335-37.

5. F. A Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Third Edition, John Wiley and Sons, 1972, 189-91.

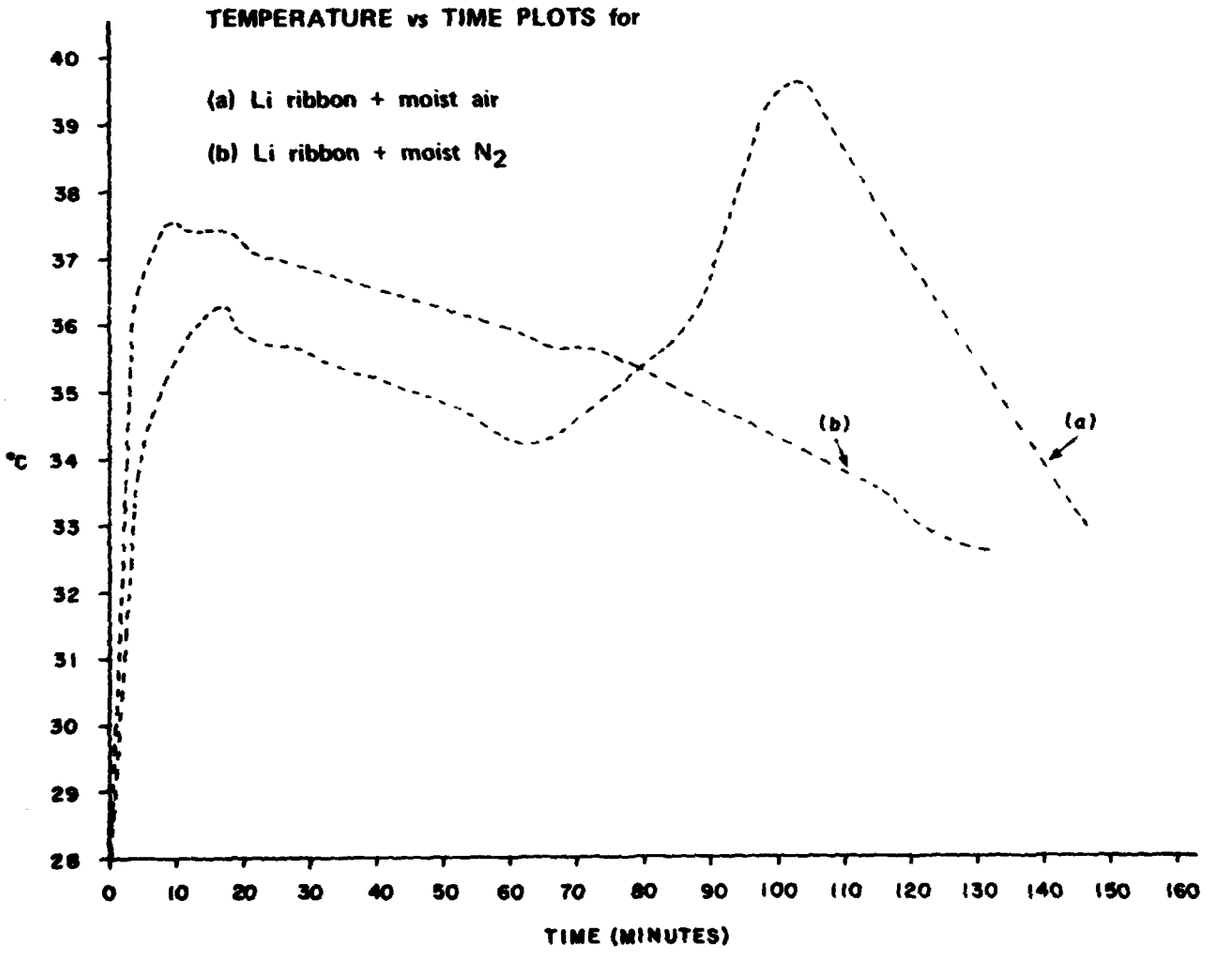

FIGURE 4. Temperature vs. Time Plots for Li Metal Reactivity With Controlled Atmospheres

The lithium metal and the $Li_{8.8}B_4$ samples obviously behaved similarly toward dry atmospheres or moist oxygen and nitrogren. However, their respective behavior toward moist air was not only very different between the two materials, but also within a sample material when compared to the other moist atmospheres. These results are of a qualitative nature, and explanations must await more quantitative data.

6. RENOVATION/MODIFICATION OF DRI-LAB

The Vacuum Atmospheres Dri-Lab renovation and modification is complete, and this facility provides a nitrogen, oxygen, and water concentration in an argon atmosphere of less than 1.0 parts per million. The facility is pictured in Figure 5. Preparation of lithium-boron compositions and study of their reactivity can now be carried out on a quantitative basis, utilizing as well the associated thermal analysis equipment to provide the data to satisfy the objectives of this program.

7. DISCUSSION OF RESULTS

The alloying process which occurs during formation of the known compound alloy of lithium and boron is very poorly understood. The appearance of a viscosity increase in the liquid phase as the temperature of the solution increases is unique, as is the formation of a solid phase at high temperatures. Also, the nature of the exothermic process in the solid is poorly characterized as a function of composition. The existence of other compound alloys is unexamined, and the obtainment of a compound alloy in powder form is certainly a desirable objective. Finally, a phase diagram for the lithium-boron system must be obtained now that the solubility of boron in lithium has been demonstrated.

With respect to the air reactivity of compound alloys as well as simple homogeneous solutions in solid phase, a great deal more quantitative data must be obtained before the reactions with oxygen/nitrogen/moisture can be characterized and explained. It is also necessary to have an understanding of the similarly based reactivity of lithium metal to use as a

FIGURE 5. Dri-Lab Facility

1. Dri-lab enclosure
2. Oxygen concentration monitor
3. Thermal analysis control/monitor
4. Nitrogen getter column

The oxygen getter column is located under the dri-lab enclosure.

comparison and standard for discussions of reactivity of compound alloys. The anomalous double exotherm during humid air reaction of lithium is particularly problematic, as is the maximum temperature difference observed for lithium-boron compositions as a function of lithium percentage. Thus, a great deal of information must be gathered before adequate explanations of the chemistry of this new and exciting alloy system can be stated.

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